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The results from a collaborative test of U.S. EPA Method 13A and 13B are presented. The collaborative test was conducted at a primary aluminum reduction plant. In the collaborative test, six laboratories each operated two Method 13 sampling trains and all laboratories simultaneously sampled the same stack. Ten such sampling runs were done for a total of 120 samples. Each source sample was analyzed for fluoride using both Method 13A and Method 13B. The results of the collaborative test showed that both test methods gave similar results.

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COLLABORATIVE STUDY OF EPA METHOD 13A AND METHOD 13B

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ABSTRACT

Described are the results from a collaborative test of U.S. Environmental Protection Agency Method 13 at a primary aluminum plant. This test method is used to measure the fluoride emissions from primary aluminum plants and phosphate fertilizer plants. In the collaborative test, six laboratories simultaneously sample the same stack using two Method 13 sampling trains for a total of twelve Method 13 samples per sampling run. Ten such sampling runs were accomplished for a total of 120 samples. Each source sample was analyzed for fluoride content using Method 13A (SPANDNS spectrophotometric procedure) and Method 13B (ion selective electrode procedure).

The collaborative test results showed that the two methods gave similar results. The within-laboratory standard deviation in milligrams fluoride per cubic meter for Method 13A was 0.044 and for Method 13B was 0.037. Similarly, the between-laboratory standard deviation for Method 13A was 0.064 and for Method 13B was 0.056. These estimates include sampling and analysis error.

Based on the analysis of aqueous fluoride samples by each collaborator, the bias in milligrams of fluoride per liter was -0.08 for Method 13B and -0.10 for Method 13A.

Also presented in the report are precision estimates for the two methods in terms of repeatability and reproducibility. A discussion of how to use these collaborative test results for evaluating source testing results is also given.

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SECTION 1

INTRODUCTION

The Environmental Protection Agency (EPA) requires that the fluoride emissions from phosphate fertilizer plants and aluminum reduction plants be sampled using the Method 13 sampling train which is shown in Figure 1.[1,2,3] Further, unless it can be shown to the satisfaction of the Administrator that the fluoride is completely water soluble and can be accurately analyzed without distillation, these EPA regulations require that the samples collected be fused with sodium hydroxide and distilled from sulfuric acid prior to analysis. In effect, this means that most phosphate fertilizer plants can analyze their samples without fusion and distillation, but that the aluminum plants must subject their samples to the fusion and distillation procedures before analyzing them for fluoride. The regulations permit analysis by either the SPADNS spectrophotometric analytical procedure (Method 13A) or the ion selective electrode analytical procedure (Method 13B).

Previous work performed on aluminum plant and phosphate fertilizer plant samples by Mitchell and Midgett[4] determined that the fusion and distillation procedures were the predominant source of imprecision in the Method 13 analytical procedures. Thus, the challenge that the Method 13 analytical procedures would receive from aluminum plant samples would be much more severe than the one it would receive from phosphate fertilizer plants. In addition, the fluoride emissions from aluminum plants are also much lower in concentration

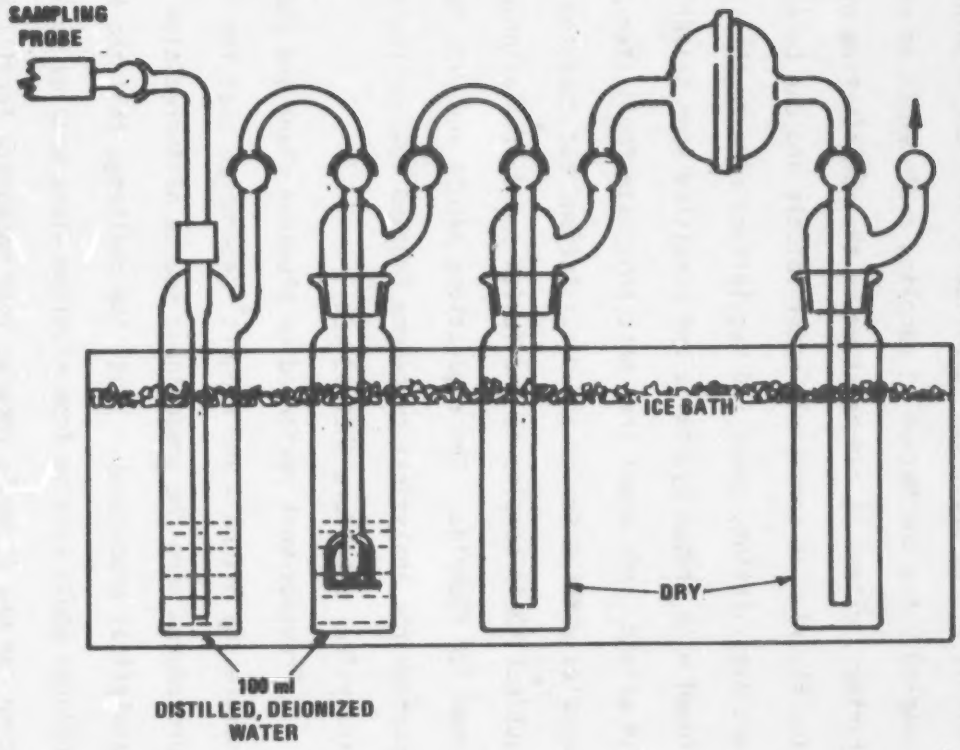

Figure 1. Method 13 sampling train

than those from fertilizer plants. Thus, the sample recovery technique should receive a more severe challenge at an aluminum plant than at a phosphate fertilizer plant. For these reasons, we decided that the best place to adequately evaluate Method 13 through a collaborative test would be at a primary aluminum reduction plant.

However, the cyclic nature of the primary aluminum reduction process, itself, causes the fluoride concentration in the stack to fluctuate with time. Thus, the Environmental Protection Agency (EPA) regulations applicable to primary aluminum reduction plants[2] require that the potroom emissions be sampled for a minimum of eight hours per sampling run using the Method 13 sampling train (Figure 1). These regulations also require that the stack cross section be divided into equal concentric areas and that each area be sampled for an equal period of time during the eight hours of sampling. This latter requirement, which is termed traversing the stack, is employed because the fluoride concentration also may not be homogeneously distributed across the stack cross section.

Now, the objective in conducting collaborative testing of a source test method is to determine the performance of the method when it is used by qualified laboratories. Further, a primary requisite for a collaborative test is that all laboratories sample and analyze essentially identical samples. This is because the precision of the method is frequently determined from a statistical comparison of the results obtained by each of the collaborators to the mean obtained on that sample by all the collaborators. Also, to ensure that the estimates of precision obtained are reliable, it is usually required that the precision estimate obtained have at least 30 degrees of freedom associated with it.[5]

Because of: (1) the above requirements for a collaborative test; (2) the non-homogeneity in the fluoride concentration across the stack; (3) the random fluctuations in the fluoride concentration over an eight hour time interval; and (4) the unusually long sampling time required by the regulation, it was evident that it would not be cost-efficient to use the standard collaborative test techniques previously developed for collaboratively testing stationary source test methods[6,7,8] to conduct a collaborative test of Method 13. The eight hour sampling time alone would require about three weeks of field testing to obtain a statistically adequate number of samples. And of course, the unstable nature of the fluoride concentration in the stack with time and with position would make it tenuous to assume that samples taken at the same point in the stack but at different times would be statistical replicates.

Thus, we decided to employ the four train sampling arrangement previously developed and field tested by Mitchell and Midgett.[4,9] This technique, which employs fixed-point sampling has been shown to yield essentially statistical replicates when applied to stacks in which a fluctuating or non-homogeneous pollutant concentration exists. For the collaborative test of Method 13, we employed six laboratories and three, four train sampling arrangements. Ten, 3-hour sampling runs were accomplished with each laboratory operating two sampling trains in each run, for a total of 12 samples per run. Two runs were accomplished each day.

SECTION 2

SUMMARY AND CONCLUSIONS

This report presents the results of a collaborative test of the U.S. Environmental Protection Agency (EPA) Method 13 that was conducted at a primary aluminum plant. The collaborative test employed six laboratories with each laboratory simultaneously operating two identical Method 13 sampling trains in each of ten sampling runs. Since each laboratory simultaneously sampled the stack, a total of twelve replicate samples per run were obtained.

At the conclusion of the collaborative test each test participant returned his samples to his own laboratory for analysis for fluoride. In the laboratory each sample was fused with sodium hydroxide and distilled from sulfuric acid. Then aliquots from each distillate were analyzed by Method 13A (SPADNS spectrophotometric procedure) and by Method 13B (ion selective electrode procedure). In this manner, estimates of the within-laboratory and the between-laboratory precision of Methods 13A and 13B (including sampling error) were obtained.

Estimates of the accuracy of Methods 13A and 13B were obtained by having each collaborating laboratory perform duplicate analyses on an aqueous sodium fluoride standard solution. These samples were fused and distilled as described in the methods.

The precision and accuracy estimates obtained are delineated below. Unless otherwise noted, these precision estimates include sampling error and pertain to the determination of a single sampling run result and not to the

average of three results that is specified in the performance test for compliance section of the Federal Register:

Method 13A

The within-laboratory standard deviation — σ = 0.044 mg fluoride per standard cubic meter with 60 degrees of freedom — was estimated from the difference between the two trains that were operated by the same laboratory and was determined to be independent of fluoride concentration in the range measured. The between-laboratory standard deviation— σ_L = 0.064 mg fluoride per standard cubic meter with 5 degrees of freedom — was estimated from the within-run differences between the results of the six participating laboratories. The bias in the analytical procedure — based on the analysis of the standard fluoride sample — was determined to be -0.10 mg fluoride per liter.

Method 13B

The within-laboratory standard deviation — σ = 0.037 mg fluoride per standard cubic meter with 60 degrees of freedom — was estimated from the differences between the two trains that were operated by the same laboratory and was determined to be independent of fluoride concentration in the range measured. The between-laboratory standard deviation— σ_L = 0.056 mg fluoride per standard cubic meter with 5 degrees of freedom, was estimated from the within-run differences between the results of the six participating laboratories. The bias in the analytical procedure — based on the analysis of the standard fluoride sample — was determined to be -0.08 mg fluoride per liter.

An alternate way to report precision of a test method is in terms of Mandels'[5] repeatability (a measure of the within-laboratory precision) and reproducibility (a measure of the between-laboratory precision). For our purposes, repeatability will be defined as a quantity that will be exceeded

only about 5 percent of the time by the difference, taken in absolute value, of two randomly selected test results obtained by the same laboratory on replicate samples. Reproducibility will be defined as a quantity that will be exceeded only about 5 percent of the time by the difference, taken in absolute value, of two single test results made on identical samples by two different laboratories, that is, two labs sampling at the same port.

Thus, if we define a test result as a single sampling run, the repeatability of Methods 13A and 13B is 0.123 mg fluoride per dry standard cubic meter and 0.102 mg fluoride per standard cubic meter, respectively. The analogous reproducibility estimates are 0.259 mg fluoride per standard cubic meter and 0.241 mg fluoride per standard cubic meter.

SECTION 3

DESIGN OF THE COLLABORATIVE TEST

The collaborative test was designed so that the six laboratories each operated two Method 13 sampling trains identical to the one shown in Figure 1. All laboratories sampled for fluoride at an isokinetic sampling rate at a point very near the center of the stack.

The sampling arrangement used in the test involved three sets of clustered sampling trains. Each cluster consisted of four Method 13 sampling trains, two "S" type pitot tubes, and two laboratories. The pairing of the laboratories was switched between runs, so that each laboratory was paired-up with every other laboratory twice during the collaborative test. Further, each sampling train was operated independently of the other trains with the exception that the two trains operated by the same laboratory used the same pitot tube for setting and maintaining an isokinetic rate.

Table I shows the location of each laboratory in each of the ten runs and Figure 2 shows the orientation of the sampling ports. By employing this test design, it is possible to obtain reliable estimates of the within-laboratory and between-laboratory precision of Method 13.

Because the sampling, fusion and distillation procedures of the Methods 13A and 13B analytical procedures are identical, it was possible to obtain separate estimates of the precision of Method 13A and of Method 13B using the same source sample. This was accomplished by having each laboratory take

every source sample through the fusion/distillation procedure and then analyze separate aliquots from the distillate using the SPADNS (Method 13A) and the ion selective electrode (Method 13B) procedures.

Estimates of the accuracy of the two analytical methods were obtained by giving each laboratory two identical aqueous samples of sodium fluoride to analyze using the complete Method 13A and Method 13B analytical procedures.

TABLE 1. SAMPLING LOCATION ASSIGNMENTS BY COLLABORATOR NO.

	SOUTH PORT		WEST PORT		NORTH PORT	
Run No.	A	B	C	D	E	F
1	104	105	102	101	106	103
2	104	102	105	103	106	101
3	102	105	101	103	104	106
4	102	106	101	105	104	103
5	103	102	106	105	104	101
6	106	102	105	101	103	104
7	105	102	103	101	106	104
8	102	104	103	105	101	106
9	105	104	101	102	103	106
10	102	103	105	106	101	104

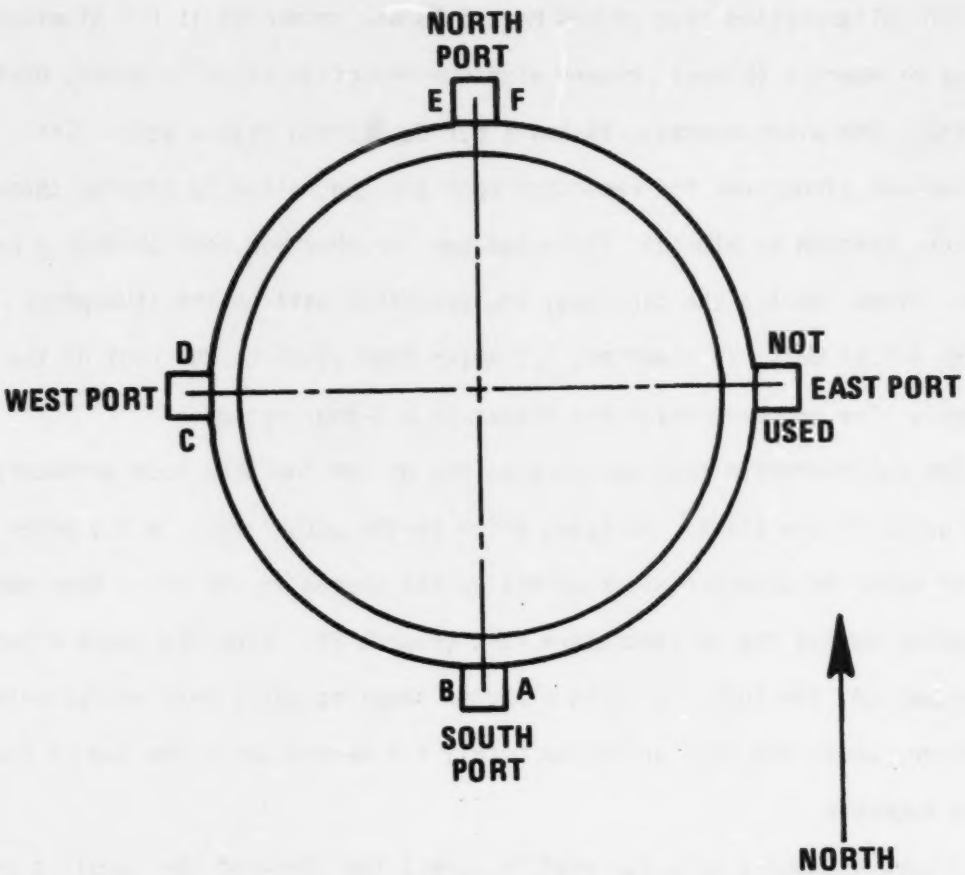

Figure 2. Sampline Port Locations.

SECTION 4

COLLABORATIVE TEST SITE

The collaborative test of EPA Method 13 was conducted at the Aluminum Company of America (Alcoa) primary aluminum reduction plant in Badin, North Carolina. The plant operates 24-hours per day, seven days a week. The fluoride emissions from its reduction pots are controlled by passing these emissions through an alumina, fluidized-bed scrubber and then through a baghouse. After leaving the baghouse, the emissions exit to the atmosphere through a 1.67 meter in diameter, 1.7 meter high stack on the roof of the baghouse. The baghouse units are shaken on a 3-hour cycle.

The collaborative test was done on one of the fourteen such scrubber/baghouse units at the plant. However, prior to the actual test, a 2.6 meter long by 1.67 meter in diameter stack extension was placed on the stack that was to be sampled during the collaborative test (Figure 3). When the stack extension was installed, the four, 15 cm in diameter sampling ports were approximately 1.9 meters above the roof or approximately 4.5 meters above the top of the bags in the baghouse.

Figure 4 shows a velocity profile across the stack at the sampling ports. This profile was obtained just prior to the first sampling run in the collaborative test. During the collaborative test the twelve sampling nozzles were located very near the center of the stack. The twelve meter boxes were located on the catwalk that is attached to the side of the baghouse building

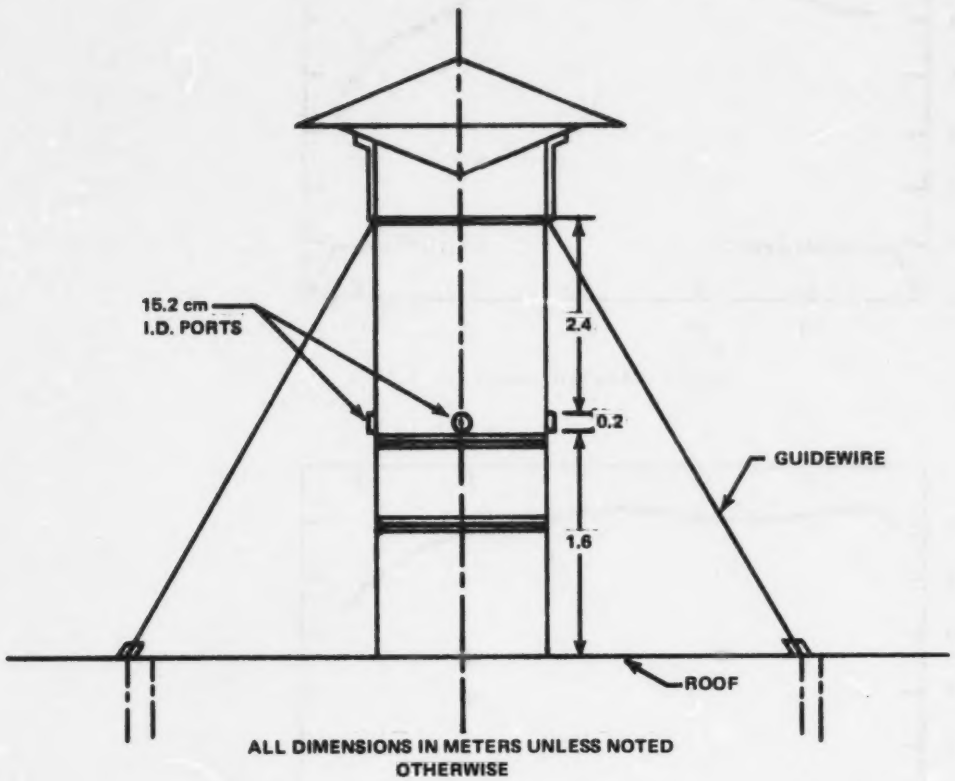

Figure 3. Stack Extension.

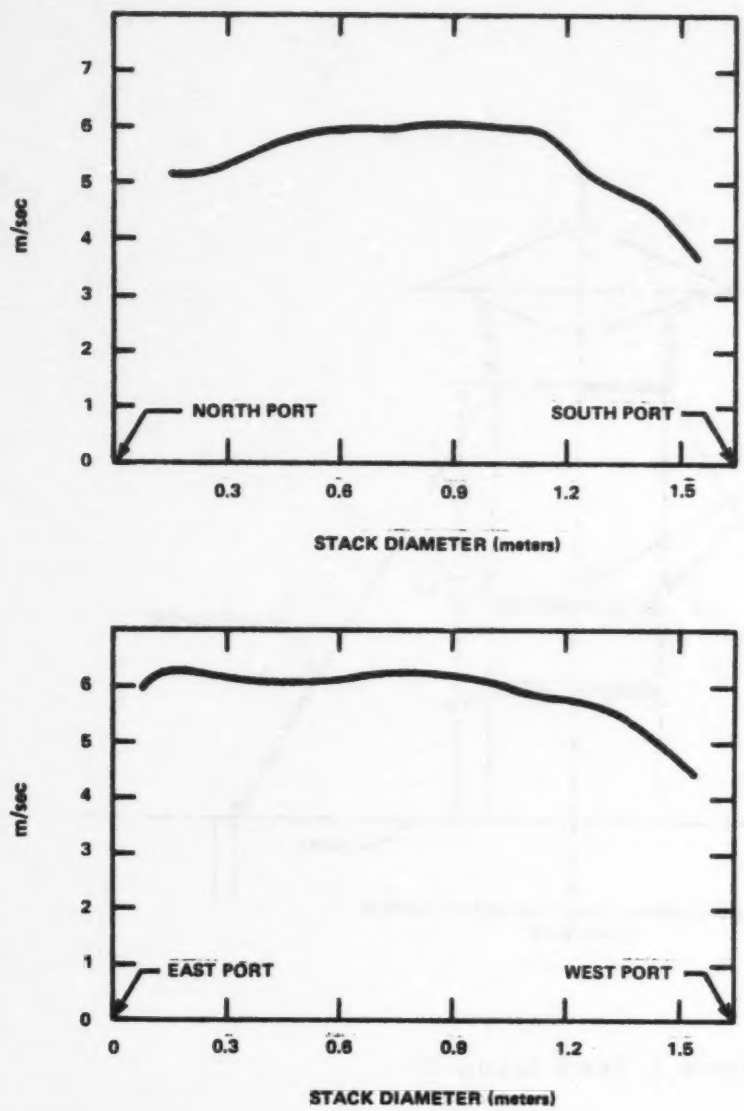

Figure 4. Velocity Profile in Stack.

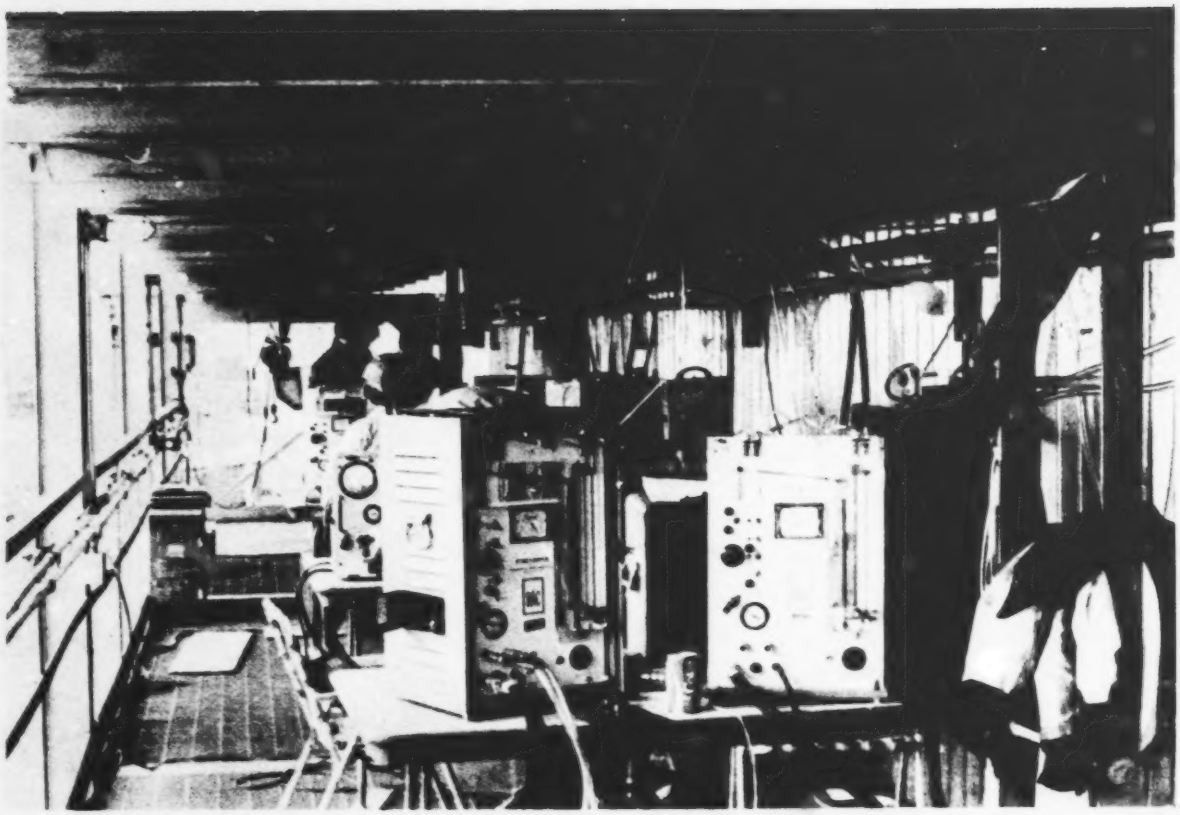

Figure 5. Control Consoles on Catwalk 4.6 Meters Below Roof

about 4.6 meters below the roof line (Figure 5). The roof of the baghouse building extends over the entire width and length of the catwalk. The catwalk itself is accessible by means of a 21.5 meter aluminum rung, cage enclosed ladder. Access to the roof from the catwalk is accomplished by means of a 4.6 meter aluminum rung ladder that extends through a hole cut in the roof.

During the collaborative test the equipment was transported from the ground to the catwalk using an electric-powered hoist. The equipment was then manually moved from the catwalk to the roof through the hole cut in the roof for the 4.6 meter ladder.

SECTION 5

SELECTION OF COLLABORATORS

The six laboratories that participated in the collaborative test were selected from a list of 25 laboratories who had expressed interest in participating in the collaborative test. To qualify for consideration as a participant each of these 25 laboratories was required to analyze four fluoride - containing samples using at their option either Method 13A (SPADNS spectrophotometric procedure) or Method 13B (ion selective electrode) and submit the analytical results with their estimate of what it would cost for them to participate in the collaborative test. Each fluoride sample was fused with sodium hydroxide and distilled from sulfuric acid prior to analysis by the above analytical procedures. The thirteen laboratories that actually analyzed the samples were compensated for the cost of the analysis to a maximum of $125.00.

The analytical results submitted by these thirteen laboratories were subjected to a comparative statistical analysis and those laboratories that demonstrated competence with the Method 13 analytical procedure were ranked on the basis of cost. The six lowest bidders were then selected to participate.

COLLABORATORS

The collaborators who participated in the sampling part of the collaborative test of Method 13 were:

Name	Organization
John Haslbeck Billy McCoy	T.R.W. Environmental Engineering Vienna, VA
David Huckabee Frank Phoenix	Entropy Environmentals Inc. Raleigh, NC
Fred Lucree Joseph Wilson	Scott Environmental Technology Plumsteadville, Pa.
Dale Huddleston Jeff Bishop	Aluminum Company of America Pittsburgh, Pa.
Larry Meyers Glenn Walden	Kaiser Aluminum and Chemical Company Pleasanton, Ca.
Pete Watson Kim Thompson	Commonwealth Laboratories, Inc. Richmond, Va.

NOTE: Throughout the remainder of this report, the collaborating laboratories are referenced by randomly assigned code numbers as Lab 101 through Lab 106. These code numbers do not necessarily correspond to the above ordered listing of collaborators.

The collaborative test was conducted under the general supervision of Mr. Fred Bergman of Midwest Research Institute, Kansas City, Missouri and Dr. William J. Mitchell, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Research Triangle Park, North Carolina 27711. They had the overall responsibility for assuring that the test was conducted in accordance with the collaborative test plan and that the collaborators adhered to the Method 13 sampling procedure. They were assisted by Mr. Nick Stich of Midwest Research Institute.

SECTION 6

TEST EQUIPMENT

EQUIPMENT SPECIFICATIONS

The impinger and filter holder portion of the two trains that were operated by the same laboratory were placed in a paired-train sampling box similar to that shown in Figure 6. Each box was 35.5 cm long by 45.7 cm wide by 33.0 cm high.

The dimensions of the sampling probes used in the collaborative test are shown in Figure 7. The four probes and two pitot tubes used in each sampling cluster were held in place by the probe clamp assembly shown in Figure 8.

Figure 9 shows the top and side view of an assembled sampling cluster. The slotted angle scaffolding and the roller assembly on which the sampling cluster was moved into and out of the stack are shown in Figures 10 and 11. Figure 12 shows the location and orientation of the twelve sampling nozzles in the stack itself.

Figures 13 and 14 show views of the impinger transport boxes and the probe transport boxes, respectively. Each probe transport box could hold 16 sampling probes and each impinger transport box could hold two paired-train boxes.

The other equipment used in the collaborative test is delineated in the bid package and follow-up letter sent to each participant. The bid package is reproduced in Appendix A.

PRETEST CALIBRATION REQUIREMENTS

Improper calibration of test equipment and changes in the calibration factor after laboratory calibration and prior to the test can be sources of error in stack testing programs. To minimize the chance for miscalibrated or out-of-calibration equipment to affect the test results, the collaborators were required to provide Midwest Research Institute with the calibration

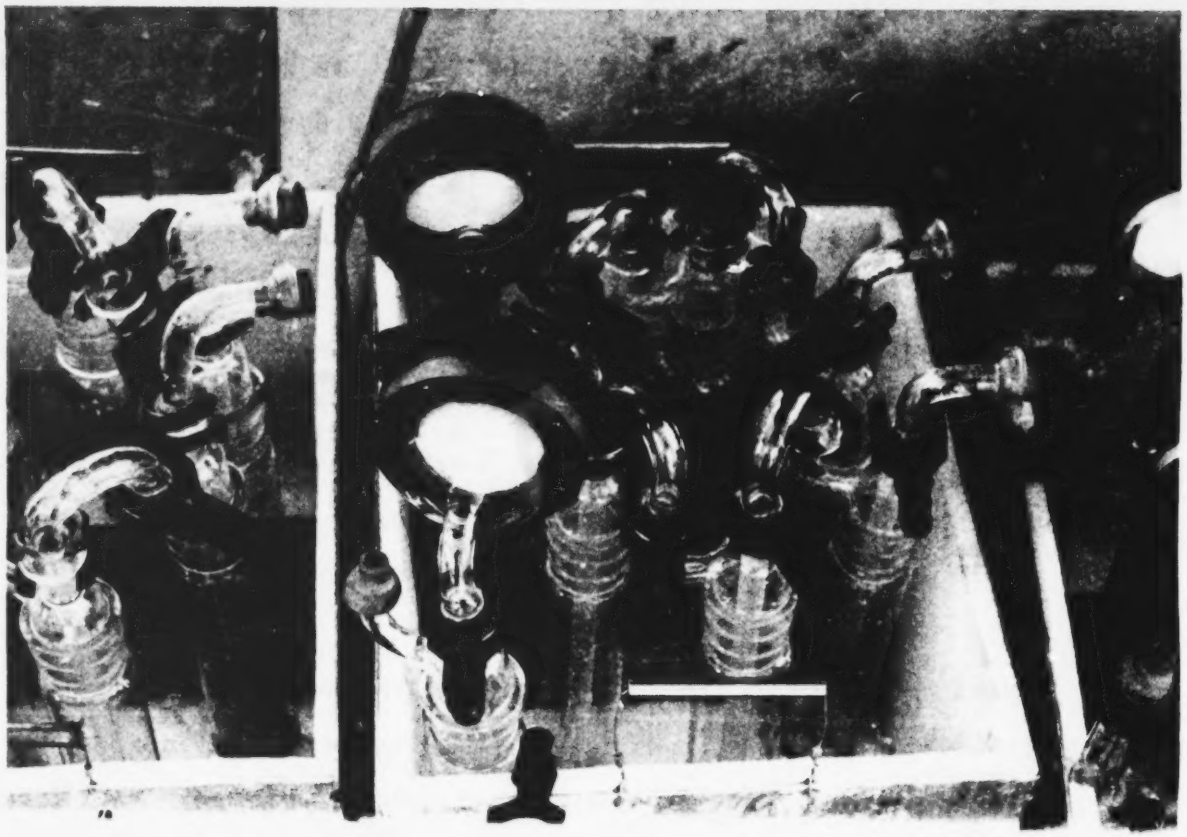

Figure 6. Paired Train Sampling Box

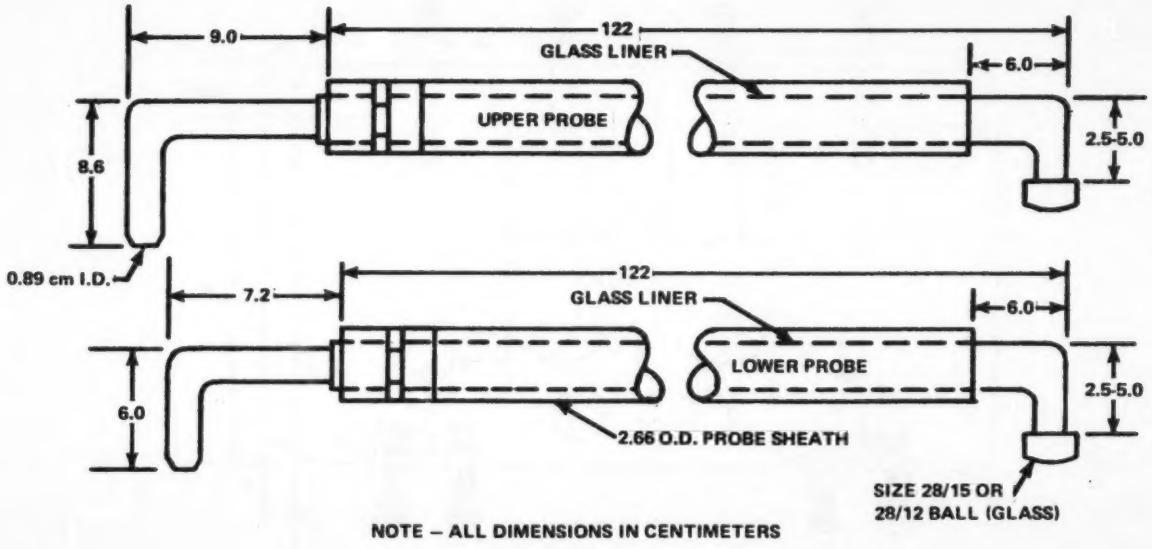

Figure 7. Upper and Lower Sampling Probes.

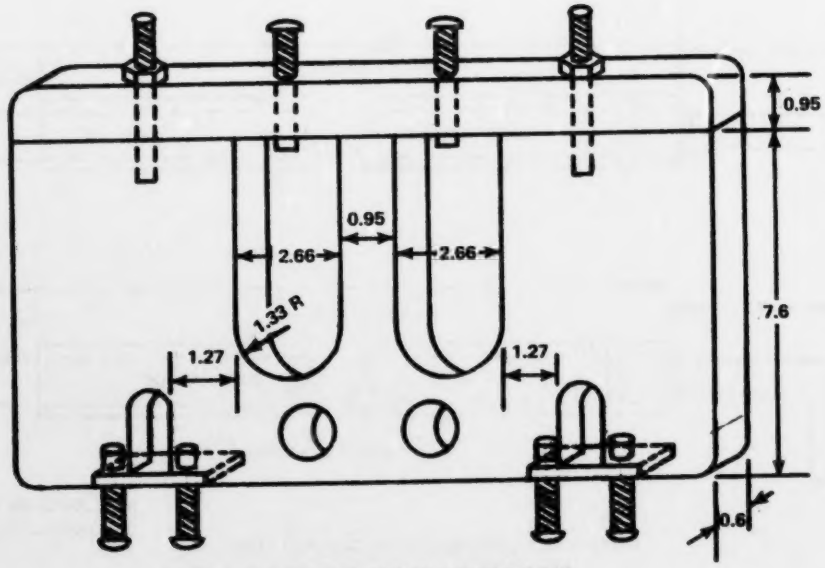

Figure 8. Probe Clamp. (2 per Cluster).

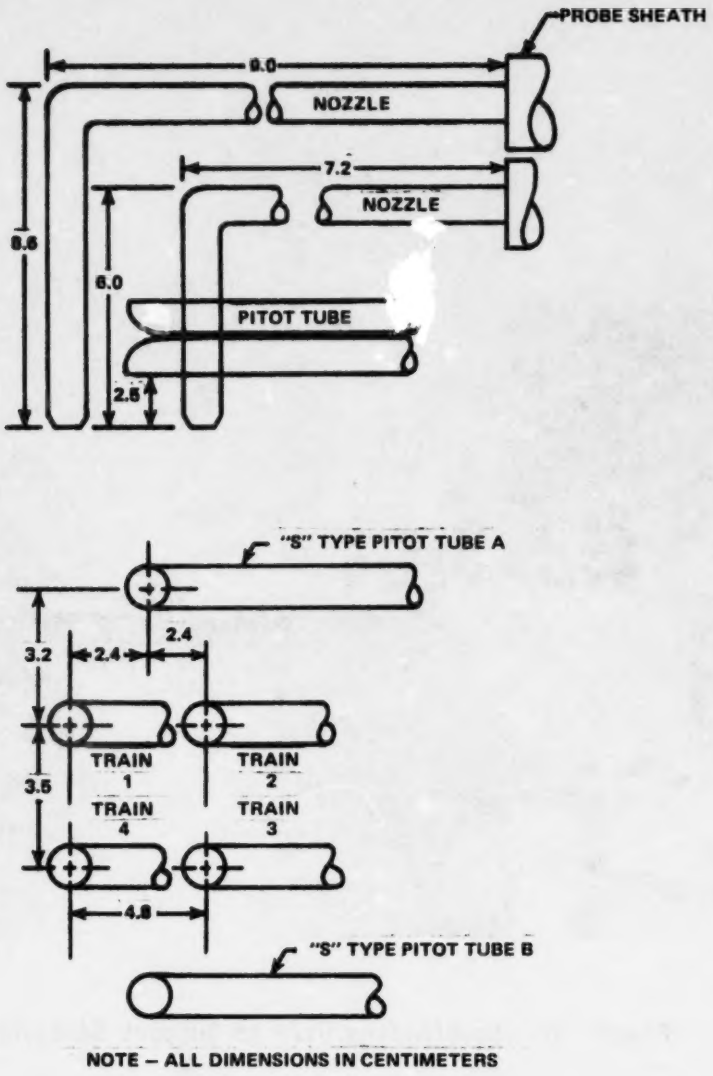

Figure 9. Double Pitot Sampling Arrangement: (Top) Side View; (Bottom) Upstream View.

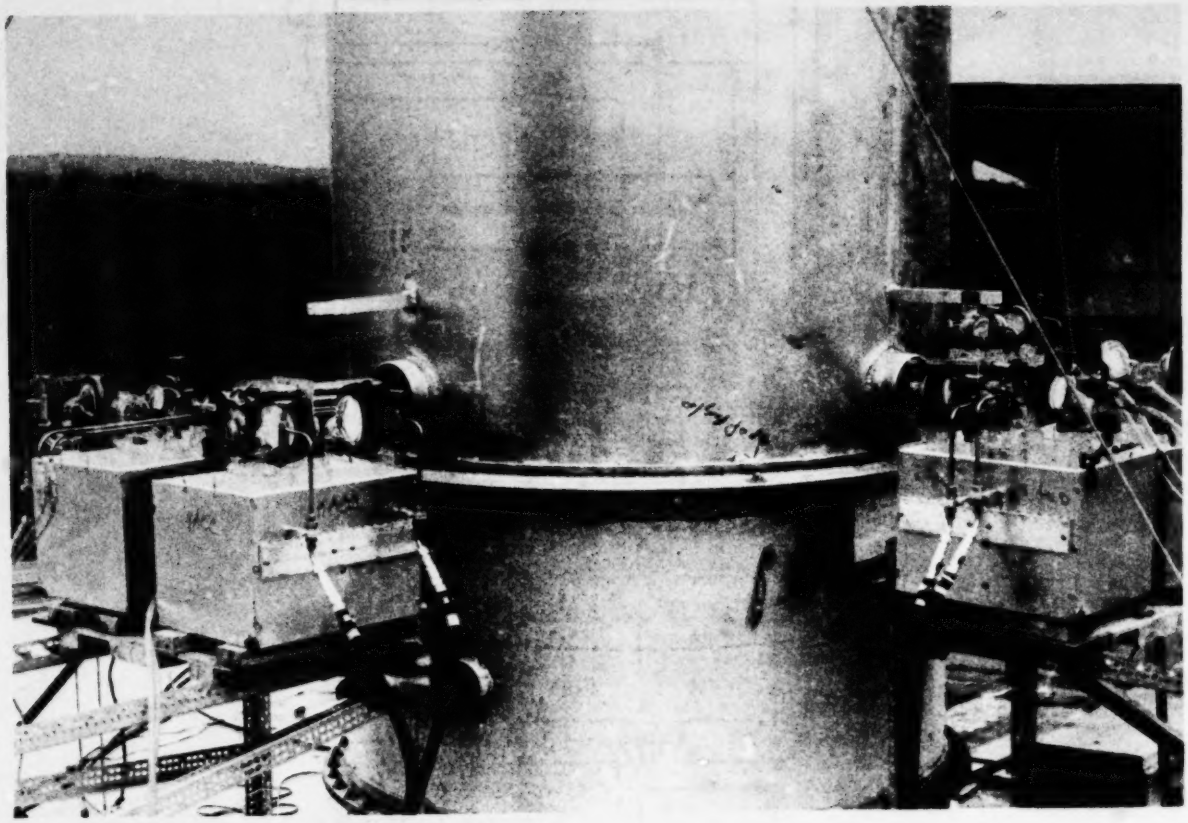

Figure 10. Scaffolding Used to Support Sampling Assembly.

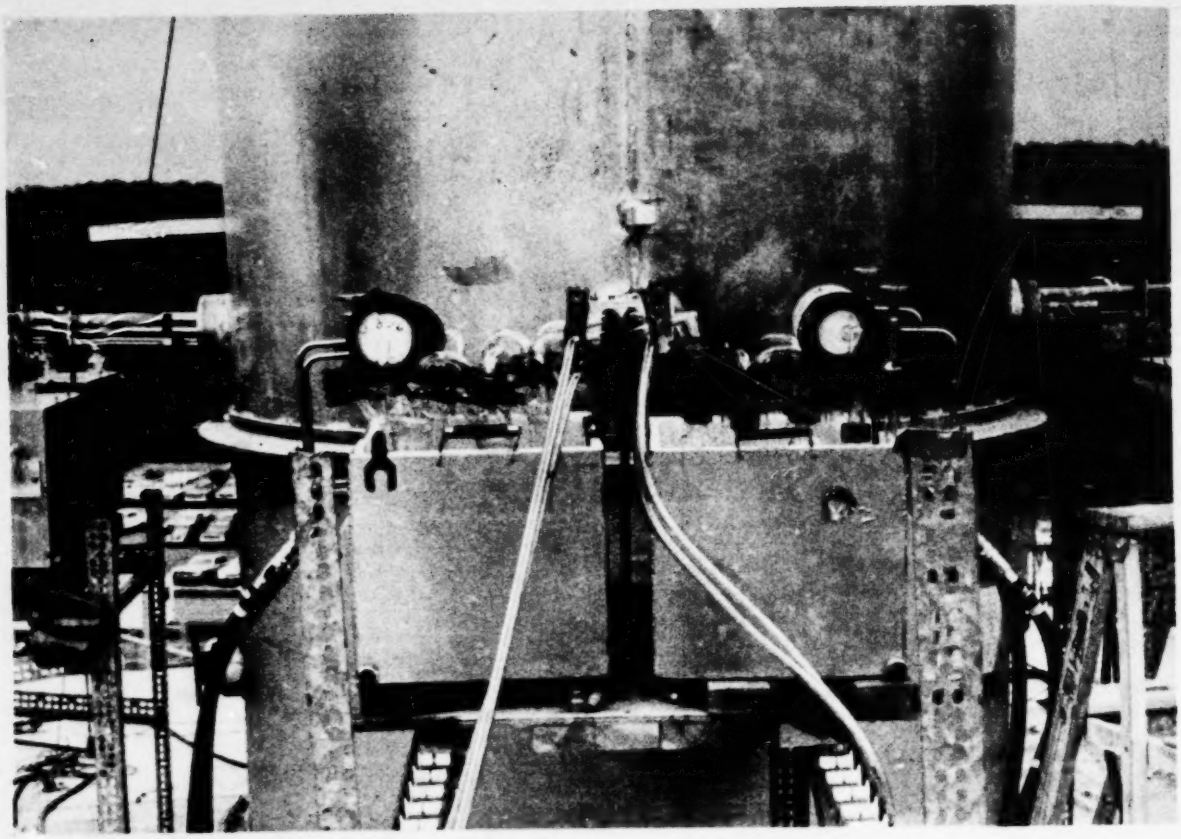

Figure 11. Roller Assembly for Moving Sampling Assembly Into Stack

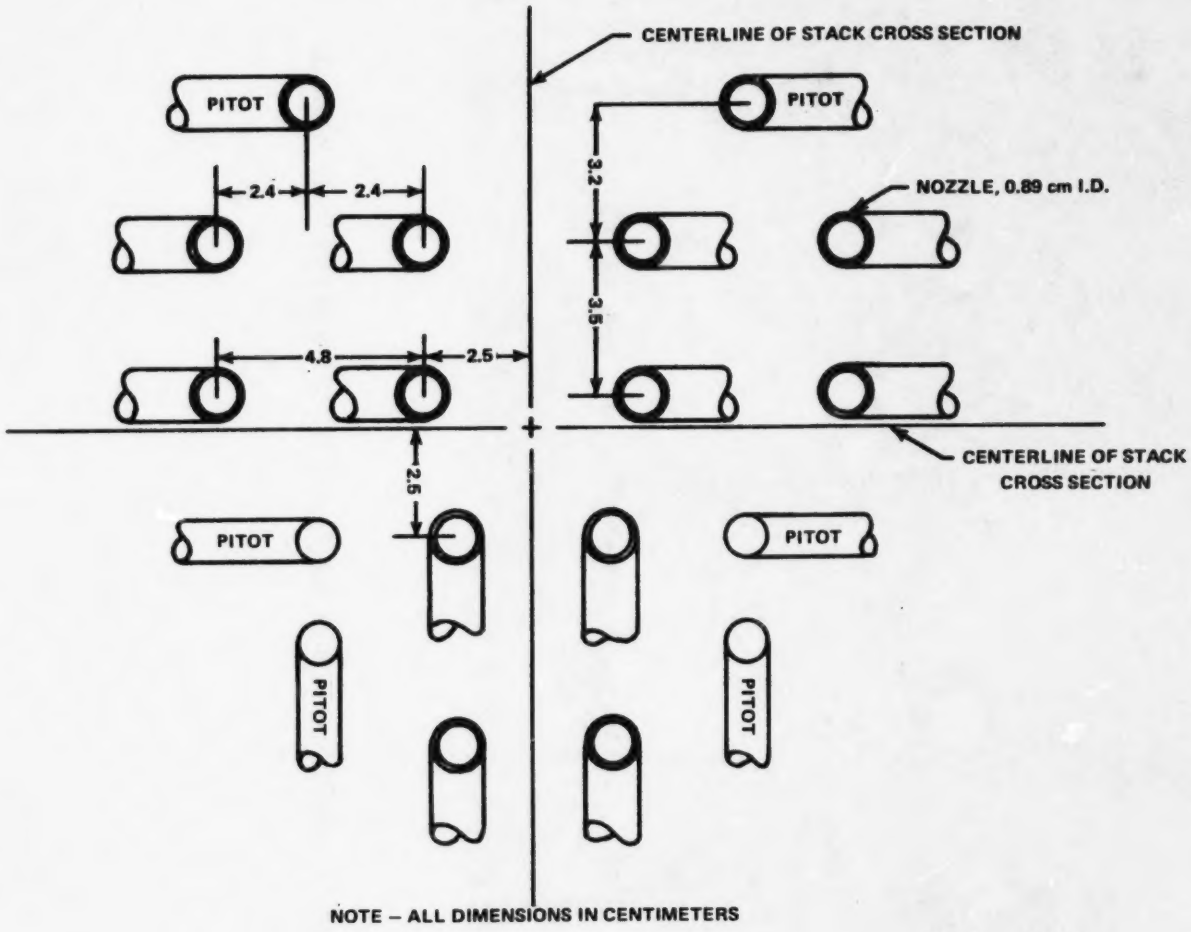

Figure 12. Nozzle and Pitot Orientation During Sampling.

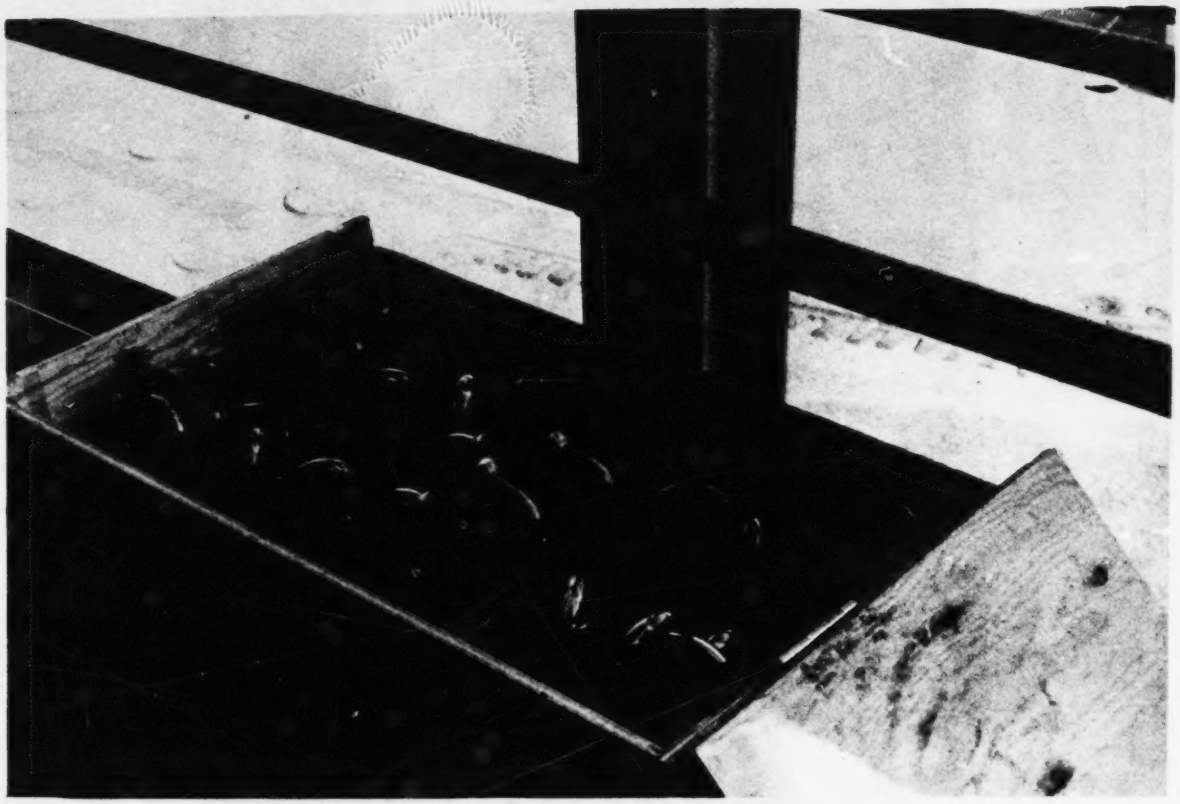

Figure 13. Impinger Transport Box with Two Paired Train Boxes

Figure 14. Probe Transport Box

factors for their "S" type pitot tube, nomographs and control consoles prior to the start of the test. The console calibrations were carried out as specified by Rom[10], the pitot tubes were calibrated in the absence of the sampling probe as described in the proposed Revised Method 2[11]; and the accuracy of the nomographs was checked using the method of Shigehara[12].

As a further check on the console calibration and to determine if any changes in calibration had occurred during shipment, each console was subjected to a two-point calibration check at the U.S. Environmental Protection Agency, Environmental Research Center, Research Triangle Park, North Carolina. The calibration check was done using either a 600 liter spirometer or a dry gas meter that had been calibrated against the spirometer. The results are presented in Table 2.

The control consoles were checked at orifice pressure drops of 1.8 and 3.0 inches of water, which was the expected range to be used during the collaborative test.

Only the two consoles operated by Collaborator 105 were found to be significantly out of calibration for both the orifice calibration and the dry gas meter calibration (Table 2). These two meter boxes were adjusted and recalibrated against the spirometer. All the other control consoles were found to be within the presently allowed specifications for the dry gas meter coefficient (γ = 1.00 $\pm$ 0.02), but three of these consoles had stated orifice coefficients that differed by more than $\pm$ 5% from the value determined in the EPA laboratory. The respective collaborators recalibrated these three consoles against the spirometer and used this recalibrated value in the collaborative test.

Prior experience had shown that commercially available nomographs are not always reliable, due to misalignment of the various scales on the nomo-

TABLE 2. METER BOX CALIBRATION CHECK RESULTS

Collaborator Number	Box Number	Orifice Coefficient		Gas Meter Coefficient	
		Found	Stated	Found	Stated
101	1	1.65	1.63	0.991	0.982
	2	1.65	1.73	0.980	0.995
102	1	2.09	1.93	0.989	0.99
	2	2.12	1.93	0.980	1.00
103	1	2.05	1.86	1.005	1.01
	2	2.01	1.92	0.995	1.00
104	1	1.72	1.73	1.01	0.995
	2	1.73	1.74	0.999	0.992
105	1	1.95	2.27	1.07	0.991
	2	1.53	1.85	1.09	0.992
106	1	1.73	1.64	1.00	0.994
	2	1.63	1.70	0.993	0.99

graphs. Thus, prior to shipping their equipment each collaborator was instructed to check the accuracy of his nomographs by the method of Shigehara[12]. Further, to preclude an inaccurate nomograph from accidently being used in the collaborative test, each laboratory was assigned a problem to be worked using his nomographs at the EPA laboratory. The results of this nomograph check showed that all nomographs were within acceptable accuracy.

The pitot tubes to be used in the collaborative test were checked in the EPA laboratory to be sure they were not physically deformed or dented and to ensure that the thermocouple was not within 1.9 cm (0.75 inches) of the pressure sensing ports.

After the calibration and equipment checks were completed the equipment was placed in a truck and transported to Badin, North Carolina — a distance of approximately 183 km (110 miles) from Research Triangle Park, North Carolina.

Equipment Leak Check

Fully-assembled sampling trains were leak-checked by plugging the tip of the probe nozzle with a septum and pulling a 370 torr vacuum on the entire train. To pass the leak check, the leak rate under these conditions had to be less than 0.0006 m^3/min.

In this manner each train was leak-checked before insertion into the stack and immediately after removal from the stack.

SECTION 7

CONDUCT OF THE COLLABORATIVE TEST

Fixed-point stack sampling was employed in the collaborative test. In each run, the sampling tip of each nozzle was located no further than 8 cm from the center of the stack. Each sampling cluster consisted of four Method 13 sampling trains, two "S" type pitot tubes and two laboratories (Figure 9). Within each cluster each laboratory monitored the stack velocity using their own "S" type pitot tube and sampled at an isokinetic rate with two of the four trains in that cluster. For example, if Laboratories 101 and 102 were using the sampling arrangement shown in Figure 9, Laboratory 101 would use trains 1 and 2 and pitot tube A and Laboratory 102 would use trains 3 and 4 and pitot tube B.

All twelve sampling trains (4 trains per cluster, 3 clusters) simultaneously sampled for fluoride. This was accomplished by inserting the first cluster through the north port, the second cluster through the south port, and the third cluster through the west port of the stack (Figure 2). The actual pairing of laboratories within a cluster varied from run to run to ensure that every laboratory was paired-up with every other laboratory twice during the collaborative test.

Of course, with twelve sampling trains sampling within a rectangular area 16 cm by 13 cm, physical blockage of the stack or misalignment of the sampling clusters could adversely affect the velocity determinations by one or more of the pitot tubes.

To determine if physical blockage of the stack area would affect the velocity measurement, the following study was done before the actual collaborative test was initiated:

(1) An isolated "S" type pitot tube was inserted through the east port and positioned so that its pressure sensing ports were at the center of the stack.

(2) The velocity head measured by the isolated pitot tube was monitored as the three sampling clusters were inserted into the stack and located in the position they would have during the collaborative test.

(3) The velocity head measured by the isolated pitot tube was also monitored as the sampling clusters were rapidly withdrawn from the stack.

No blockage effect was found, that is, the velocity head measured by the isolated "S" type pitot tube was not visually affected by the presence of the three sampling clusters.

To preclude misalignment of the sampling clusters from occurring during the test, the following procedure was followed before each sampling run:

(1) The nozzle/pitot orientations were visually checked before the sampling clusters were inserted into the stack.

(2) The first cluster was inserted through the north port and positioned near the center of the stack.

(3) Then as the second cluster was brought into position through the south port, the velocity head measured by the two pitots in the other cluster was monitored.

(4) Finally, as the third cluster was brought into position through the west port, the velocity head measured by the two pitot tubes nearest the west port was compared to the appropriate velocity head measured by the two pitot

tubes nearest the east port.

(5) After all clusters were inserted, the test supervisor made a visual inspection of the orientation of the clusters in the stack by looking through the unused east port. (It should be noted that in no case was the velocity head measured within a cluster affected as the other clusters were inserted. This demonstrates that physical blockage of the stack was not significant enough to affect the velocity.)

At the conclusion of the first run of that day, the twelve sampling probes were placed in the probe transport box (Figure 14). Similarly, two, paired-train sampling boxes were placed in each impinger transport box (Figure 13). After the sampling trains for the second run were assembled, leak-checked and inserted into the stack, the probes and impinger boxes from the first run of that day were moved in their respective transport boxes to the clean-up trailers on the ground. At the end of the second run for that day, the impinger boxes and the probes from this run were placed in transport boxes and moved to the ground. All sample train assembly, disassembly and sample recovery operations were done in trailers located near the base of the stack.

By utilizing the above sampling scheme the work scheduled for each day was achieved in about 10-1/2 hours.

At the conclusion of the collaborative test, the recovered samples were returned to the participating laboratories for analysis by Methods 13A and 13B. That is, each source sample was fused and distilled using the Method 13 procedure and aliquots from the same distillate were analyzed by both the SPADNS spectrophotometric procedure (Method 13A) and the fluoride ion selective electrode procedure (Method 13B).

As a means to check the accuracy of the analysis, each collaborating laboratory was also given two aqueous sodium fluoride standard solutions that contained two mg fluoride per liter and were instructed to analyze these samples using the complete Methods 13A and 13B. Since both samples were identical in concentration, the results of these analyses are actually a duplicate analysis on identical samples. However, the collaborators were not aware that the two samples were identical, nor were they aware that the samples contained only sodium fluoride.

SECTION 8

STATISTICAL ANALYSIS OF THE RESULTS

Precision

For the statistical analyses, the six laboratories were randomly designated as Labs 101, 102, 103, 104, 105 and 106. The collaborative test consisted of ten sampling runs with twelve samples collected in each run for a total of 120 samples. Each source sample was fused and distilled and then separate aliquots from each sample were analyzed for fluoride using Methods 13A and 13B. In addition, each laboratory analysed two aqueous sodium fluoride standard solutions that each contained 2 mg fluoride per liter.

The actual sampling results reported by each laboratory are presented in Table 3 (Method 13A) and Table 4 (Method 13B). The analytical results on the fluoride standard solution are reported in Table 5. The results in Tables 3, 4 and 5 were checked for calculation errors and no significant errors were found.

The results in Tables 3 and 4 were subjected to an analysis of variance (ANOVA) to determine the precision of the two methods. Precision of the methods deals with the differences between observations made under similar conditions as determined by the experimental design. For the purpose of the ANOVA, the results in Tables 3 and 4 were considered to have been gathered using a balanced, incomplete block design. The design was considered incomplete in the sense that a sampling port could accommodate only two laboratories in a sampling run. With 15 possible laboratory pairings from six laboratories and with three ports avail-

TABLE 3. SAMPLING RESULTS FOR METHOD 13A IN mg F/DRY STD. M^3.

Run No.	Train Position	Pair 1 Port A	Pair 1 Port B	Pair 2 Port C	Pair 2 Port D	Pair 2 Port E	Pair 3 Port F
1		Lab 104	Lab 105	Lab 102	Lab 101	Lab 106	Lab 103
	front	0.19	0.32	0.22	0.27	0.24	0.23
	rear	0.21	0.29	0.24	0.30	0.23	0.20
2		Lab 104	Lab 102	Lab 105	Lab 103	Lab 106	Lab 101
	front	0.18	0.23	0.33	0.36	0.33	0.18
	rear	0.19	0.23	0.35	0.35	0.26	0.29
3		Lab 102	Lab 105	Lab 101	Lab 103	Lab 104	Lab 106
	front	0.81	1.18	0.87	1.18	0.88	0.87
	rear	0.84	1.16	1.00	1.12	0.80	0.90
4		Lab 102	Lab 106	Lab 101	Lab 105	Lab 104	Lab 103
	front	0.77	1.07	1.06	1.40	1.10	1.04
	rear	0.76	1.02	1.11	1.29	1.14	1.23
5		Lab 103	Lab 102	Lab 106	Lab 105	Lab 104	Lab 101
	front	0.47	0.43	0.46	0.64	0.56	0.52
	rear	0.47	0.44	0.57	0.67	0.56	0.51
6		Lab 106	Lab 102	Lab 105	Lab 101	Lab 103	Lab 104
	front	0.45	0.34	0.60	0.45	0.40	0.49
	rear	0.40	0.20	0.50	0.56	0.43	0.38
7		Lab 105	Lab 102	Lab 103	Lab 101	Lab 106	Lab 104
	front	0.46	0.39	0.52	0.38	0.32	0.22
	rear	0.41	0.32	0.48	0.51	0.37	0.33
8		Lab 102	Lab 104	Lab 103	Lab 105	Lab 101	Lab 106
	front	0.32	0.39	0.59	0.61	0.33	0.36
	rear	0.35	0.44	0.68	0.59	0.36	0.35
9		Lab 105	Lab 104	Lab 101	Lab 102	Lab 103	Lab 106
	front	0.35	0.33	0.41	0.32	0.33	0.30
	rear	0.34	0.25	0.41	0.34	0.42	0.27
10		Lab 102	Lab 103	Lab 105	Lab 106	Lab 101	Lab 104
	front	0.26	0.41	0.49	0.41	0.34	0.33
	rear	0.27	0.45	0.49	0.44	0.37	0.32

TABLE 4. SAMPLING RESULTS FOR METHOD 13B IN mg F/DRY STD. M^3.

Run No.	Train Position	Pair 1 Port A	Pair 1 Port B	Pair 2 Port C	Pair 2 Port D	Pair 2 Port E	Pair 3 Port F
1		Lab 104	Lab 105	Lab 102	Lab 101	Lab 106	Lab 103
	front	0.25	0.32	0.24	0.27	0.21	0.23
	rear	0.21	0.29	0.24	0.30	0.23	0.20
2		Lab 104	Lab 102	Lab 105	Lab 103	Lab 106	Lab 101
	front	0.24	0.25	0.33	0.36	0.29	0.18
	rear	0.23	0.23	0.36	0.35	0.25	0.19
3		Lab 102	Lab 105	Lab 101	Lab 103	Lab 104	Lab 106
	front	0.96	1.18	0.81	1.18	0.90	0.80
	rear	0.86	1.16	0.92	1.14	0.90	0.87
4		Lab 102	Lab 106	Lab 101	Lab 105	Lab 104	Lab 103
	front	0.77	0.97	1.00	1.40	1.10	1.01
	rear	0.92	1.00	1.02	1.29	1.16	1.23
5		Lab 103	Lab 102	Lab 106	Lab 105	Lab 104	Lab 101
	front	0.46	0.45	0.50	0.64	0.57	0.50
	rear	0.47	0.46	0.55	0.67	0.56	0.51
6		Lab 106	Lab 102	Lab 105	Lab 101	Lab 103	Lab 104
	front	0.40	0.37	0.60	0.48	0.39	0.47
	rear	0.38	0.32	0.50	0.52	0.45	0.38
7		Lab 105	Lab 102	Lab 103	Lab 101	Lab 106	Lab 104
	front	0.46	0.39	0.51	0.40	0.35	0.24
	rear	0.42	0.33	0.49	0.47	0.36	0.39
8		Lab 102	Lab 104	Lab 103	Lab 105	Lab 101	Lab 106
	front	0.38	0.41	0.60	0.64	0.32	0.36
	rear	0.39	0.44	0.67	0.59	0.34	0.33
9		Lab 105	Lab 104	Lab 101	Lab 102	Lab 103	Lab 106
	front	0.36	0.33	0.41	0.35	0.33	0.27
	rear	0.34	0.23	0.37	0.35	0.42	0.26
10		Lab 102	Lab 103	Lab 105	Lab 106	Lab 101	Lab 104
	front	0.32	0.40	0.50	0.42	0.32	0.33
	rear	0.31	0.45	0.49	0.43	0.35	0.38

TABLE 5. ANALYSIS OF UNKNOWN STANDARD SOLUTION (2 mgF/ℓ).

Collaborative No.	Method 13A	Method 13B
101	1.80	1.89
	1.64	1.73
102	1.90	1.85
	1.90	1.80
103	2.01	1.97
	2.01	1.97
104	2.00	2.20
	1.80	2.00
105	1.93	1.90
	1.85	1.80
106	2.08	1.98
	1.87	1.90

able for each run, five sampling runs were needed to do the experiment. The entire experiment was then repeated.

A linear model for this experiment is:

$$Yijkl = \mu + RUN_i + PORT\ (RUN)_{j(i)} + LAB_k + ERROR_{l(ijk)}$$

where

μ = a constant,

RUN_i = runs effect (random) i = 1,2----, 10,

$PORT\ (RUN)_{j(i)}$ = sampling port effect (random) j = 1,2,3,
Even though the ports remain stationary, the effect may change randomly with each run,

LAB_k = laboratory effect (random) k = 1,2,3,4,5,6

$ERROR_{l(ijk)}$ = residual error (random). In the analysis of variance for this model, the error is split into two parts: intra-port error and sub-sampling error. Intra-port error is a measure of the difference between laboratories sampling through the same port. Sub-sampling error is the difference in the two measurements made by the two sampling trains operated by the same laboratory. Of course, the analytical portion also contributes to the error, but there is no way of separating this from sampling error.

In an experiment of this type, primary interest centers on estimating variance components. The analysis of variance results and the expected mean squares for Methods 13A and 13B are presented in Tables 6 and 7, respectively. (The actual statistical analysis and an explanation of the terms is presented in Appendix B.)

TABLE 6. ANALYSIS OF VARIANCE AND VARIANCE COMPONENT ESTIMATION (METHOD 13A)

Source	D.F.	S.S.	M.S.	EMS
Run	9	8.7930	.97770	$\sigma^2 + 2\sigma_I^2 + 4\sigma^2_{P(R)} + 12\sigma^2_R$
Port (Run)	20	.6860	.03430	$\sigma^2 + 2\sigma_I^2 + 4\sigma_P^2{}_{(R)}$
Lab (adj. for port effects)	5	.2825	.05650	$\sigma^2 + 2\sigma_I^2 + 20(.6)\sigma_L^2$
Intra-port Error	25	.1786	.00714	$\sigma^2 + 2\sigma_I^2$
Subsampling Error	60	.1182	.00197	σ^2
Total:	119	10.0583		

TABLE 7. ANALYSIS OF VARIANCE AND VARIANCE COMPONENT ESTIMATION (METHOD 13B)

Source	D.F.	S.S.	M.S.	EMS
Run	9	8.6501	.9611	$\sigma^2 + 2\sigma^2_I + 4\sigma^2_{P(R)} + 12\sigma^2_R$
Port (Run)	20	.6039	.0302	$\sigma^2 + 2\sigma^2_I + 4\sigma^2_{P(R)}$
Lab (adj. for port effects)	5	.2279	.0456	$\sigma^2 + 2\sigma^2_I + 20(.6)\sigma^2_L$
Intra-port Error	25	.1836	.0073	$\sigma^2 + 2\sigma^2_I$
Subsampling Error	60	.0819	.00137	σ^2
Total:	119	9.7474		

TABLE 8. PRECISION ESTIMATES OF METHODS 13A and 13B.

Variance Components		Method 13A	Method 13B
Subsampling	(σ^2)	.00197	.00137
Intra-Port	(σ_I^2)	.00259	.00297
Laboratory	(σ_L^2)	.00411	.00319
Port	($\sigma_{P(R)}^2$)	.00679	.00573
Standard Deviations of Differences Between Single Observations			
Within-Laboratory:	$\sigma_d = \sqrt{2}\sigma$	.063	.052
Between-laboratory:			
1. Same port	$\sigma_{dL} = \sqrt{2}\sqrt{\sigma^2 + \sigma_I^2 + \sigma_L^2}$	.132	.123
2. Different ports	$\sigma_{dPL} = \sqrt{2}\sqrt{\sigma^2 + \sigma_I^2 + \sigma_L^2 + \sigma_{P(R)}^2}$	.176	.162

The precision of a test method deals with the closeness of observations repeated under similar circumstances and is measured by the standard deviation of the differences. These standard deviations are reported in Table 8 and are defined in Appendix B.

Accuracy

To determine the accuracy of the analytical procedures in Methods 13A and 13B, the true value of 2.0 mg fluoride per liter was substracted from the values reported in Table 5. Then a one-way ANOVA was performed on the results to determine the accuracy.

The results of this one-way ANOVA, which are summarized in Table 9, shows that the accuracy did not change significantly from laboratory to laboratory. Although, the overall average for each method is slightly less than 2.0 mg per liter, the 95 percent confidence limit contains 2.0 mg per liter in each case. Thus, we cannot conclude that either analytical method has a significant bias.

TABLE 9. ANALYSIS OF VARIANCE OF ANALYTICAL RESULTS FROM STANDARD SAMPLE.

Method 13A					Method 13B			
Source	D.F.	S.S.	F		Source	D.F.	S.S.	F
Laboratories	5	.1005	2.062	N.S.	Laboratories	5	.1224	3.478 N.S.
Error	6	.0585			Error	6	.0423	
Total:	11	.1590				11	.1647	

N.S. = not significant at the $\alpha = .05$ level

overall mean	= 1.90 mg/ℓ
overall std. dev.	= .12 mg/ℓ
95% conf. limit for mean	[1.80, 2.00 mg/ℓ]

overall mean	= 1.92 mg/ℓ
overall std. dev.	= .12 mg/ℓ
95% conf. limit for mean	[1.83, 2.03 mg/ℓ]

SECTION 9

LIST OF REFERENCES

1. U.S. Environmental Protection Agency. "Standards of Performance for New Stationary Sources (Amendments to Reference Methods 13A and 13B)", Federal Register, 41, 52229-52230, November 29, 1976.

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4. Mitchell, W. J. and Midgett, M.R. "Adequacy of Sampling Trains and Analytical Procedures Used for Fluoride", Atm. Envir., 10, 865-872, 1976.

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APPENDIX A

BID PACKAGE SENT TO COLLABORATORS

August 16, 1976

This letter is in response to your reply to our letter dated April 2, 1976. The plans for conducting the collaborative test of EPA Methods 13A (SPADNS) and 13B (Selective Ion Electrode) have been finalized.

The test is tentatively scheduled to begin on October 12, 1976. Complete details are given in the Work Plan which is enclosed.

You have been selected as a potential participant from those responding to the original contact. If you cannot or choose not to participate in the collaborative test, please let MRI know by August 20, 1976, by calling Mr. Fred Bergman at 816-561-0202, extension 261.

The following information is addressed to those who wish to participate:

Submit to MRI no later than September 7, 1976 a firm fixed-price proposal for supplying the equipment and manpower to perform the test outlined in the enclosed Work Statement. This will include (1) fixed-price bid for the collaborative test, (2) bid for cost per day extra, (3) copies of calibration curves, and (4) analytical results.

You will be sent four (4) fluoride samples and a supply of SPADNS under separate cover. Two samples will be labeled as solid. These samples must be fused and distilled with duplicate analysis conducted on the distillate. Two samples will be labeled liquid which will require distillation and duplicate analysis. The report of the analytical results should contain the fluoride values obtained during aliquot determination (Methods 13A and 13B, Section 7.3.4) as well as the final fluoride concentration after distillation. Analysis may be conducted by utilizing either 13A or 13B. Those laboratories electing to demonstrate their analytical capabilities using both 13A and 13B will receive preference during collaborator selection over bidders using only one method. Regardless of the methods used during bidding, the use of both 13A and 13B during the collaborative test will be required. For those bidders planning on using Method 13B (SIE) it should be pointed out that the lifetime of the fluoride electrode has been found to be less than one year. SIEs older than this should be replaced before conducting the analysis.

In summary, the analysis conducted during bidding will require a total of two fusions, four distillations and eight (one method) or sixteen (two method) analysis.

To partially compensate bidders for the time spent on analysis, all bidders who submit the required analytical results will receive a fixed sum of $125.00.

If you have any questions concerning the proposed test, you may contact either Fred Bergman or Paul C. Constant at 816-561-0202.

Sincerely,

MIDWEST RESEARCH INSTITUTE

Fred Bergman

Fred Bergman
Senior Chemist

Enclosures: 5

WORK STATEMENT FOR COLLABORATIVE TEST OF EPA METHOD 13

I. Background Information

Midwest Research Institute is conducting a program on the evaluation and collaborative testing of those U.S. Environmental Protection Agency (EPA) Test Methods that apply to stationary sources. We are now making preparation to conduct the collaborative test of EPA Method 13. You are invited to submit a bid that delineates what it will cost Midwest Research Institute for you to participate in the collaborative test.

II. Test Site

The selected test site is the Alcoa primary aluminum plant in Badin, N.C. Badin is located approximately 40 miles east of Charlotte, N.C. The Alcoa plant, which operates 24-hours per day, seven days a week, controls its fluoride emissions with an alumina, dry-bed scrubber. After leaving the scrubber, the emissions pass through a baghouse before exiting to the atmosphere through a 66-in. diameter stack on the roof of the baghouse. Our collaborative test will be conducted on one of the fourteen such scrubber/bag/house units on the plant.

There is a catwalk located on the side of the baghouse at a point fifteen feet below the roof. The roof of the building extends over the entire width of the catwalk. The catwalk is accessible by means of a 70-ft aluminum rung, cage-enclosed ladder. In addition, an electric-powered hoist is available to transport equipment from the ground to the catwalk. Access to the roof from the catwalk is by means of a 15-ft aluminum ladder.

Figure A-1. Alcoa's Badin, North Carolina, Baghouse.

III. Test Plan

Fixed-point, isokinetic sampling will be employed during the collaborative test. Presently we plan to have six participating laboratories each sample simultaneously with two sampling trains for a total of twelve samples per run. Ten such sampling runs, each 3-1/2 hr in length, will be made. Two sampling runs per day will be accomplished for a total of five actual days of testing.

The sampling arrangement used in the test will involve three sets of clustered sampling trains. Each cluster will consist of four Method 13

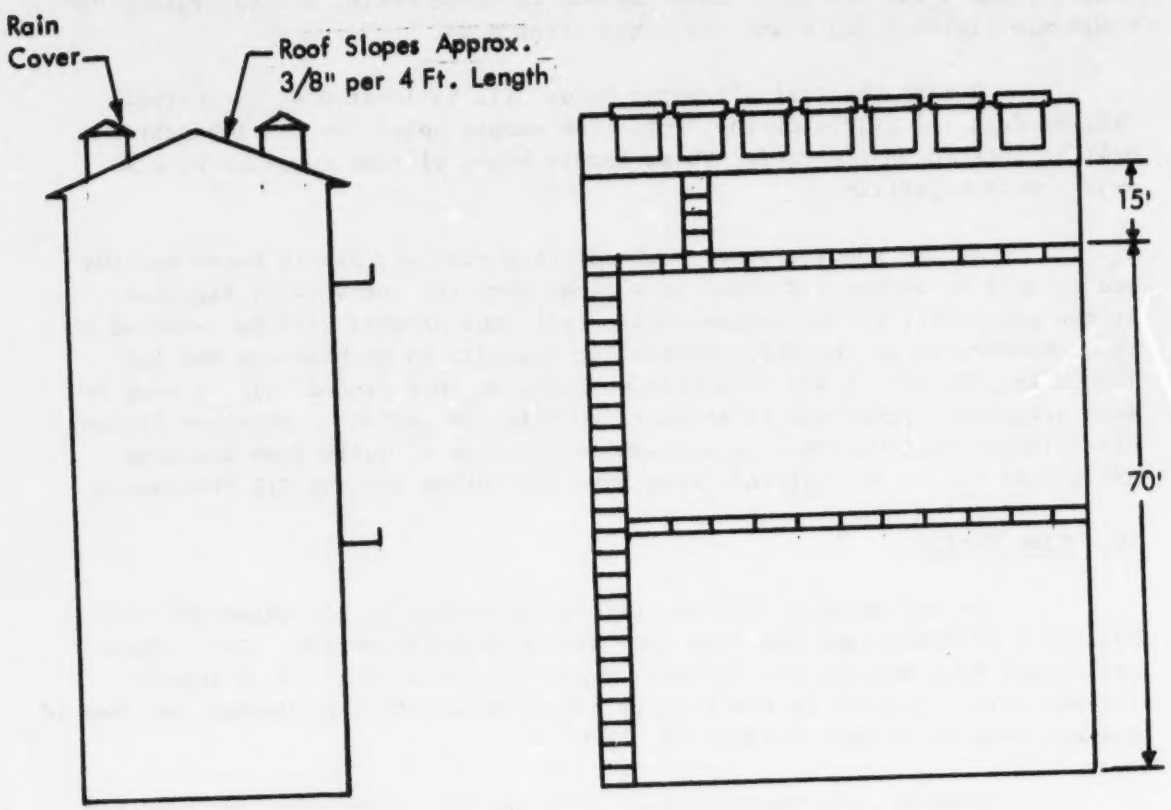

Figure A-1.. Alcoa's Badin, North Carolina, Baghouse.

sampling trains, two "S" type pitot tubes and two laboratories (Figure 2). Within a cluster each laboratory will monitor the stack velocity using one of the "S" type pitot tubes and will sample isokinetically with two of the four trains in that cluster. For example, if two laboratories, A and B, were using the sampling arrangement shown in Figure 2, Laboratory "A" would use trains 1 and 2 and the pitot tube nearest to these trains and Laboratory "B" would use trains 3 and 4 and the other pitot tube.

During the test all meter boxes will be located on the catwalk fifteen feet (15 ft) below the roof. The sample boxes for the impingers will be located on the roof. These sample boxes will be supplied by Midwest Research Institute.

At the conclusion of each sampling run, the sample boxes and the probes will be capped and moved to a clean room for recovery of fluoride. At the conclusion of the collaborative test, the samples will be returned to the laboratories of the participants for analysis by Methods 13A and 13B (including the fusion and distillation steps of this procedure). A copy of each analytical procedure is attached to this bid package. Only one fusion distillation will be required per sample, because aliquots from the same distillate are to be analyzed using both the SPADNS and the SIE procedures.

IV. Time Period

As mentioned above, the test will consist of 10, three and one-half (3-1/2) hours sampling runs made over a five-day period. This scheme will yield four samples per laboratory per day for a total of 20 samples for analysis. Testing is tentatively scheduled to start on Monday, October 18 and conclude on Friday, October 22, 1976.

However, the complexity of both the test scheme and the sampling equipment make it necessary to conduct a pre-test orientation session and a pre-test dry run. This orientation session will be held on Wednesday and Thursday, October 13 and 14, 1976, in an EPA facility in Research Triangle Park, North Carolina. At this time, the accuracy of each laboratory calibration of their meter boxes will be spot-checked against a 600-liter spirometer located in this same EPA facility.

Thursday, October 14, will be used to transport the sampling equipment to Badin, N.C. (approximately 110 miles from Research Triangle Park). It is anticipated that only one truck will be necessary to transport the equipment to Badin. Midwest Research Institute (MRI) will supply this truck. Collaborators will be expected to supply their own transportation to Badin, N.C.

Friday, October 15, will be used for equipment set-up. The dry run will also be accomplished on this day.

Table A-1 summarizes the above schedule.

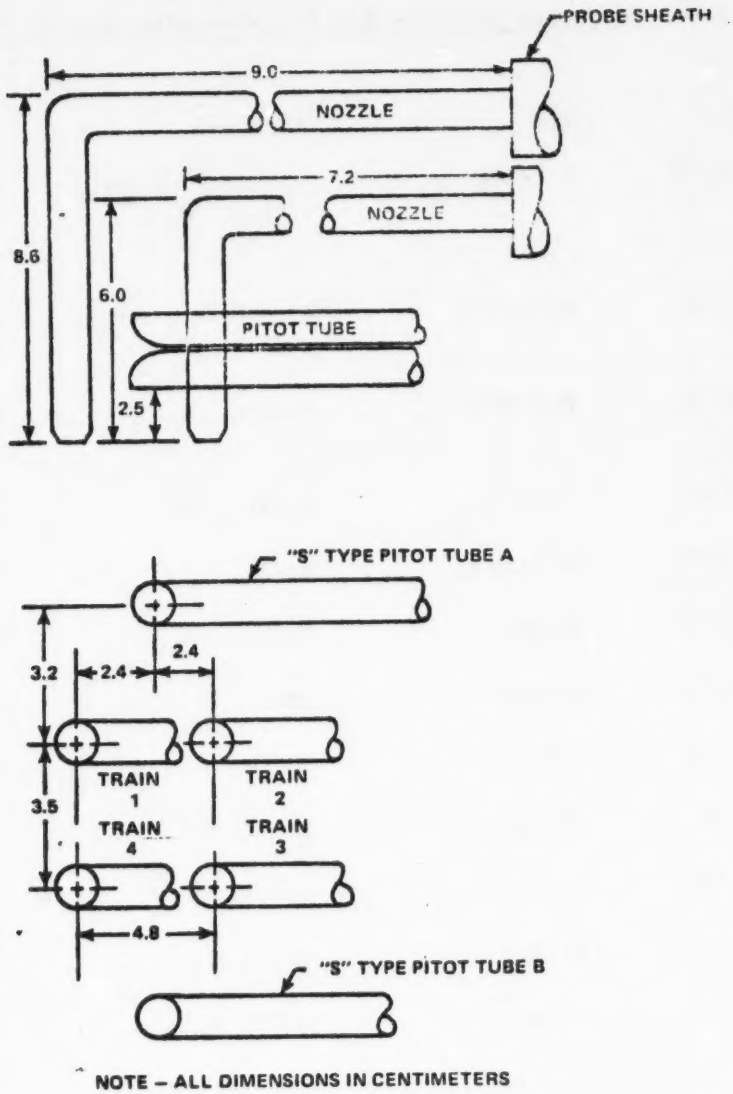

Figure A-2. Double pitot sampling arrangement: (Top) Side view; (Bottom) Upstream view.

Table A-1. Tentative Schedule for Collaborative Test of Method 13

Date	Day	Location	Activity
10/12/76	Tuesday	Research Triangle Park, N.C.	Collaborators arrive and carry equipment to the EPA facility.
10/13/76	Wednesday	Research Triangle Park, N.C.	Pre-test calibration check and orientation session.
10/14/76	Thursday	Badin, N.C.	Equipment transported to Badin, N.C.
10/15/76	Friday	Badin, N.C.	Equipment set-up and dry-run.
10/16/76	Saturday	Badin, N.C.	Open.
10/17/76	Sunday	Badin, N.C.	Open.
10/18/76	Monday	Badin, N.C.	Testing.
10/19/76	Tuesday	Badin, N.C.	Testing.
10/20/76	Wednesday	Badin, N.C.	Testing.
10/21/76	Thursday	Badin, N.C.	Testing.
10/22/76	Friday	Badin, N.C.	Testing.
10/23/76	Saturday	Badin, N.C.	Equipment disassembly.
10/25/76	Monday	Home laboratory	Start analysis.

11/76 Complete analysis and prepare final report (results of analysis and final report must be mailed to arrive at MRI on or before November 30, 1976).

V. Final Report

The final report may consist of one copy submitted in an informal letter format. It shall include as a minimum:

(1) Copies of the field test data

(2) Copies of the SPADNS and SIE calibration curves

(3) Copies of the meter box calibrations

(4) Volume and concentration of fluoride in each sample reported in µg/ml.

(5) Results of all calculation required for Method 13A and 13B (Sections 9.2, 9.3, 9.4, 9.5, 9.6, and 9.7)

(6) Names of personnel performing the sampling and conducting the analysis

(7) Description of sampling equipment (manufacturer), spectrophotometer, SIE system and any other special equipment used during the program

VI. Bid Requirements

A. Selection of Participants

Respondees to this solicitation for bids will be expected to analyze the enclosed samples for fluoride using either of the enclosed versions of EPA Method 13A (Sulfuric Acid Distillation/SPADNS) or Method 13B (Sulfuric Acid Distillation/Specific Ion Electrode). The volume of each sample will be 800 ml when shipped. The results of these analysis (in mgF/liter) and the appropriate SPADNS and/or SIE calibration curves used in the analysis must accompany the respondees bid. These bids must be received by Midwest Research Institute (MRI) not later than September 7, 1976.

Only those respondees who successfully analyze the enclosed fluoride containing samples will be considered qualified to participate in the collaborative test.

Those respondees who successfully analyze the samples will be ranked on the basis of cost and the six lowest cost bids will be selected.

B. Cost

You are requested to submit your total cost on a firm fixed-price basis for the scope of work described. This bid should include any overtime you believe will be required to maintain the test schedule. In the event that additional sampling days are required due to inclement weather, etc., you are requested to supply a cost per day for additional sampling and analysis beyond that described in the scope of work. Costs should be prepared on the basis of a two-man sampling team (2 professionals each to operate one meter box and to assist each other in sample recovery).

Resumes giving the background and qualifications of the personnel who will perform the sampling and analysis shall be included in your proposal. Since experience in the use of EPA Method 13 (which is very close to EPA Method 5) may be an important evaluation in judging the qualifications of the specified participants, their experience in using Method 13 should be included in their resumes.

VII. Equipment Required for the Test

A. Equipment to be Supplied by MRI

1. The dual train sampling box to be used by each laboratory and the necessary supporting clamps and platforms. These items will be delivered to the test site by MRI prior to the actual test.

2. Umbilical cords (1/2-in. ID).

3. Sample heads for connecting the umbilical cord to a 28/15 ball socket on the last impinger.

4. Pitot lines (3/8-in ID).

5. Nozzles - 3/8-in ID with tapered edge, 5/8 OD adapter for connecting to probe sheath.

6. Orsat analyzer (MRI will perform the Orsat analysis).

7. Cage for moving glassware up to and down from the roof.

8. Clean-up area (Two medium sized trucks).

9. Tables to set the meter boxes on.

B. Equipment to be Supplied by Collaborators

1. 2 meter box units, suitable for running Method 13, meeting the specifications described by Martin (copy attached) and calibrated as described by Rom (copy attached).

2. Three nomographs meeting the specifications described by Shigahara (copy attached). Electronic calculators may be used in place of the nomographs, but if calculators are used, back-up nomographs will be required.

3. Thirty (30) Whatman No. 1, 3 in. or 4 in. diameter paper filters (as required to fit collaborators filter holder).

4. Five matched, glass liners for sampling probes having the dimensions shown in Figure 3 with 28/12 or 28/15 male ball fitting on exit of probe and a suitable fitting on the nozzle end to accommodate a 5/8 OD nozzle. Two matched metal probe sheaths having the dimensions shown in Figure 3. Probes need not be heatable, because stack conditions do not require that the sampled gas be heated.

5. One "S" type pitot tube without thermocouple and not attached to probe sheath calibrated as described in EPA Revised Method 2 (copy attached). The pitot tube should be 42 in. long and pitot tubes with coefficients outside 0.83 to 0.87 must be calibrated as described by Shigahara.

6. The fittings necessary to connect the umbilical cords (1/2 inch ID) to the meter boxes and to connect the pitot tube line to both the pitot tube and to the meter box.

7. The usual equipment required for source testing and sample recovery, e.g., tools, extension cords, distilled water, probe brush, extra fittings, fuses, caps to fit the probes and impinger ball joints, etc.

8. Communication equipment to allow verbal communication between the team member on the roof and the team member on the catwalk during the leak-check.

9. Four complete Method 13 impinger trains each cleaned with hot soapy water and rinsed with tap water and distilled water prior to test.

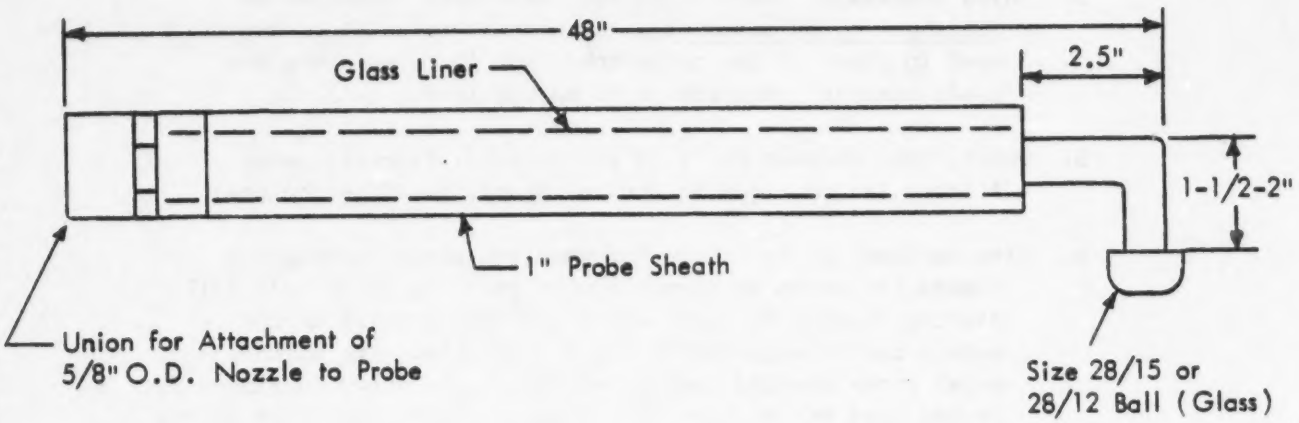

Figure A-3. Probes

10. All equipment and chemicals necessary for 13A and 13B sampling and analysis of collaborative test samples. (Analytical supplies are not required at the test site).

11. Special Conditions

The calibration data for the meter boxes and the pitot tube and also the check of the accuracy of the nomograph are to be supplied to MRI during the orientation session to be held at the EPA facility in Research Triangle Park, N.C.

APPENDIX B

STATISTICAL METHODOLOGY

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STATISTICAL METHODOLOGY

Terms and Definitions

Since the effects in the linear model used for analysis of variance in Tables 6 and 7 are random, the total variance of an observation is made up of several components:

$$\sigma^2_{Tot} = \sigma_R^2 + \sigma^2_{P(R)} + \sigma_L^2 + \sigma^2_E$$

where:

σ^2_R is the variance of the runs effects

$\sigma^2_{P(R)}$ is the variance of the ports within runs effect

σ^2_L is the variance of the laboratory effect

and,

σ^2_E is the experimental error variance component.

The last term, σ^2_E, may be further separated into two components

$$\sigma^2_E = \sigma^2_I + \sigma^2$$

where:

σ^2_I is the intra-port component of variance describing the variation contributed to an observation by its being taken in a particular port.

and,

σ^2 is the subsampling variation attributed to making repeat determinations on the same sample.

An estimate of the subsampling variation was provided without use of analysis of variance by pooling all the within-laboratory estimates of variation. The validity of pooling in this manner was checked by Bartlett's test for homogeneity of variances. (Homogeneity is a very important assumption in the analysis of variance that is summarized in Tables 6 and 7.) All the other estimates of variance components were made by equating the expected mean square columns to the mean square columns in each of Tables 6 and 7 and then solving the two systems of equations.

Combinations of variance components are useful in measuring differences between two observations. The standard deviation of the difference between two observations (analyses) by the same laboratory on the same sample will be denoted by $\sigma_d = \sqrt{2}\,\sigma$. The standard deviation between two observations each made by a different laboratory at the same port during the same run will be represented by $\sigma_{dL} = \sqrt{2}\sqrt{\sigma^2 + \sigma_I^2 + \sigma_L^2}$. The standard deviation of the difference between two observations that were each made by a different laboratory regardless of the port, but during the same run, is denoted by $\sigma_{dPL} = \sqrt{2}\sqrt{\sigma^2 + \sigma_I^2 + \sigma_L^2 + \sigma_{P(R)}^2}$.

To add a measure of probability to statements concerning differences between observations, the assumption of normality of the distribution of random effects is made.

The terms <u>repeatability</u> and <u>reproducibility</u> have become common ways of describing differences between observations with the added assumption of normality. These terms are defined for our purposes as follows:[5]

<u>Repeatability</u> —— $(\sigma_d^* = 1.96\,\sigma_d)$

—— 95 percent of the differences between two subsamples taken within a laboratory will not exceed this value in absolute value.

Reproducibility (same port) - $(\sigma_{dL}^* = 1.96\sigma_{dL})$

- 95 percent of the differences between two laboratories sampling from the same port will not exceed this value in absolute value.

Reproducibility (between ports) - $(\sigma_{dPL}^* = 1.96\ \sigma_{dPL})$

- 95 percent of the differences between two laboratories sampling from different ports will not exceed this value in absolute value.

The relationship of the distribution of differences between samples taken by two different laboratories at the same port, and by two different laboratories regardless of the port but during the same run, are represented schematically in Figure B-1. The horizontal bars indicate the 95 percent confidence limits for each of the above cases. The difference between two observations by the same laboratory but at different ports is not discussed, since this involves observations made during different runs. These differences are not of interest, because different concentration levels were encountered in different runs.

The information given in Table 8 and Figure B-1 may be interpreted as follows:

1. Two observations from the same laboratory on the same sample must differ by more than $\pm$ 0.123 mg/m^3 (Method 13A) or $\pm$ 0.102 mg/m^3 (Method 13B) to be declared significantly different (repeatability).
2. Two observations from different laboratories sampling from the same port must differ by more than $\pm$ 0.259 mg/m^3 (Method 13A) or $\pm$ .241 mg/m^3 (Method 13B) to be declared significantly different (reproducibility within ports).
3. Two observations from different laboratories sampling at different ports should differ by more $\pm$ 0.345 mg/m^3 (Method 13A) or $\pm$ 0.318 mg/m^3 (Method 13B) to be declared significantly different (reproducibility between ports).

Accuracy of the Method

Accuracy refers to the size of the deviations of estimates from the actual value (true value). Accuracy is often quantified by a term called bias. Bias is defined as the signed difference between the average of the individual estimates and the true value, that is,

$$\text{Bias} = \text{Average} - \text{True}$$

An analysis of the bias in the methodology of Methods 13A and 13B is summarized in Table 9. The chief effect of bias is to distort the probability of an estimate being in error by more than some predetermined amount. For example, when there is no bias, an estimate is expected in the long-run to exceed 1.96σ by chance alone only 5 times in a hundred, that is, 0.05. In the case of Method 13A, which has a bias of -0.10 mg/ℓ, the probability of an estimate being in error by more than 1.96σ is 0.13 and for Method 13B, which has a bias of -0.08 mg/ℓ, the probability is 0.09. These probabilities are both about twice that expected when no bias is present.

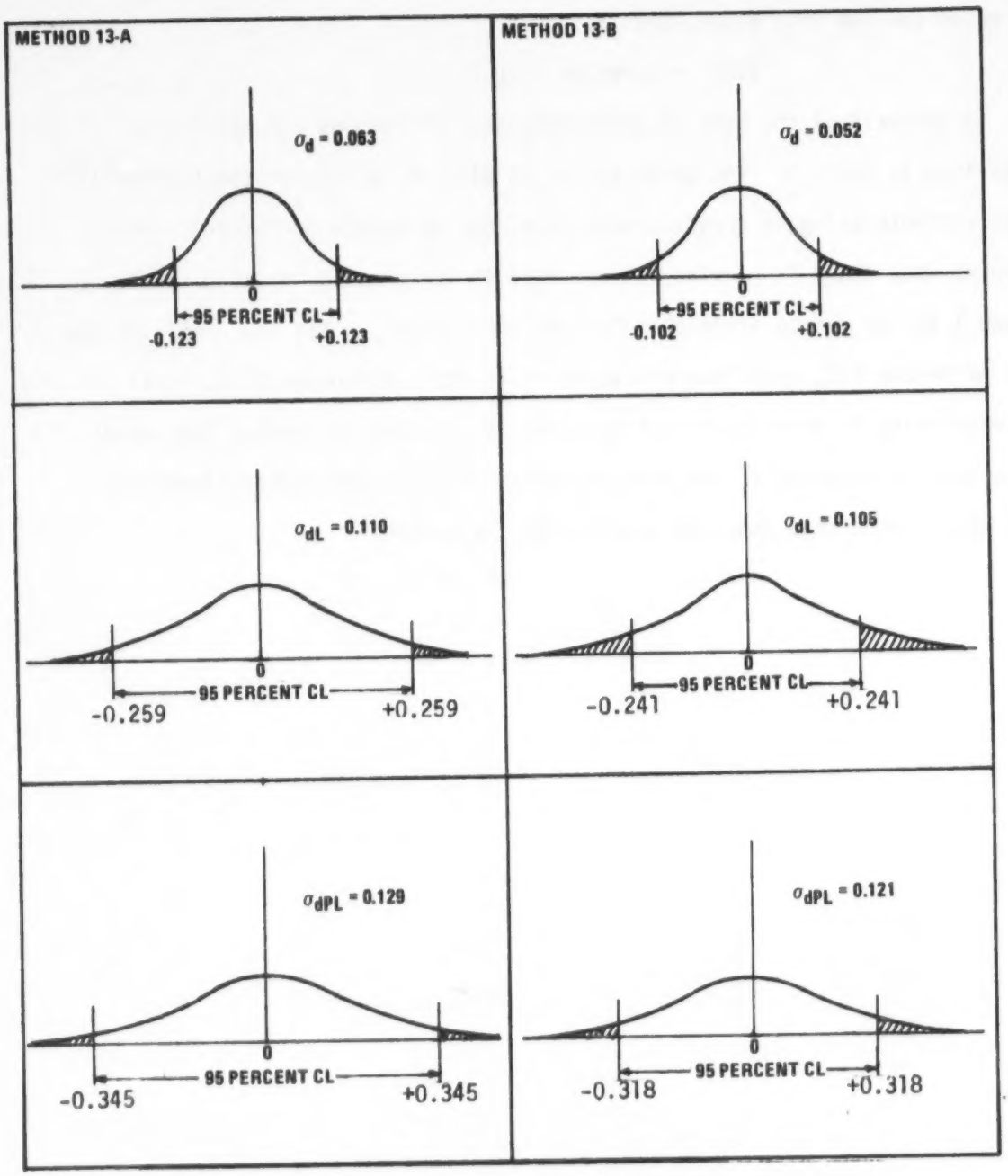

Figure B-1. Distribution Curves Corresponding to Differences.

APPENDIX C

USING COLLABORATIVE TEST DATA TO EVALUATE TEST RESULTS

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USING COLLABORATIVE TEST DATA TO EVALUATE TEST RESULTS

In source testing, it is common for one laboratory to make repeat measurements (sampling runs) on the same stack while the plant operates at constant process conditions. Under the above conditions, these repeat samples are *assumed* to be replicates, that is, they are assumed to belong to the same statistical population. Collaborative test results offer a means to determine the likelihood that these repeat measurements are truly replicates. That is, the difference between any two true replicates should lie within the limits specified by the repeatability of the measurement method as determined from the collaborative test results.

Described below are two sample techniques that can be used to determine if two repeat measurements are replicates. These two methods are illustrated using the collaborative test results from Method 13A:

Method 1:

Determine the difference between the individual sampling results and the average and compare these differences to the repeatability estimate for the method. For example, suppose Method 13A was used to sample an aluminum plant stack and the following results in mg F/m^3 were obtained:

Sampling Run No.	Sampling Result	Difference from the Average
1	0.259	0.329
2	1.024	-0.437
3	0.480	0.108
Average:	0.588	

Since the repeatability of Method 13A is $\pm$ 0.123 mg F/m^3, the results from runs 1 and 2 lie outside the value expected for Method 13A. Thus, the results do not belong to the same population and we must suspect that the stack concentration was not constant over runs or else that a significant error was made in one of the measurements.

Method 2

An alternate and quicker means to judge the homogeneity or validity of data is to employ the relative range approach. In this approach, the difference (range) between the highest and lowest values is determined and this difference (R) is then divided by the within-laboratory standard deviation (σ). Then the probability that this quotient (W) exceeds the predicted value is obtained from a Percentage Point of the Distribution of the Relative Range Table (1). For example, suppose Method 13A was used to sample a stack for fluoride and the following concentrations in mg F/m^3 were obtained:

Run 1	0.361
Run 2	0.421
Run 3	0.480

In this example, R is 0.119 (0.480-0.361) and σ is $\pm$ 0.044. Thus:

$$W = \frac{R}{\sigma} = \frac{0.119}{0.044} = 2.70$$

Since W does not exceed the predicted value for three replicates, 4.12, the test shows that the results all belong to the same statistical population.

(1) Duncan, A.J. "Quality Control and Industrial Statistics," R. D. Irwin Co., Inc., p. 908 (1965).